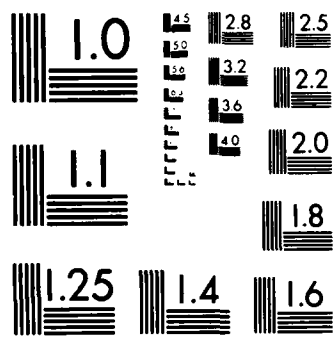


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The experimental results we developed during the course of this project, and their analyses concern the dynamics of systems undergoing intra- and inter-molecular conversions over low barriers, in the gas phase. As anticipated, for this large class of reactions, the observed relaxation times do not fully conform to the successful theories which were developed for reactions characterized by large activation energies. For some low  $E_a$  systems, departures from RRKM predictions, measured close to equilibrium conditions, indirectly provide measures of limiting IVR rates. Several intramolecular conversions (typically aziridine) and association/dissociations (typically: formic acid) were investigated.

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## COMPREHENSIVE FINAL REPORT

Unimolecular reaction rate theory, which required about three decades to become fully formulated as RRKM, is generally accepted as one of the major accomplishments of chemical kinetics. It is not an approximate solution of a realistic model; rather, it is an accurate solution of an idealized model. As developed in its present format it provides an algorithm for calculating the first order rate constant for the collision-free conversion of adequately energized molecules ( $A^*$ ) to the transition structure ( $A^\ddagger$ ), using only molecular parameters of the reacting species and of the postulated transition structure. When results of kinetic experiments are found to disagree with predictions based on an RRKM model, one of two explanations may apply:

(i) The trivial one --- the assumed mechanism may be in error. For example, a dissociation presumed to result from vibrational excitation may be due to a rate controlling displacement step followed by a rapid release of the attacking species. (ii) The more serious one --- intramolecular vibrational relaxation may be rate controlling (intrinsic non-RRKM). For example, when a substantial fraction of vibrationally excited molecules with  $E > E_a$  incorporate the energy of excitation in states which are poorly coupled to those vibrations which characterize the transition structure. One anticipates that failures of type (ii) would occur for conversions over low barriers, where the densities of vibrational states are sparse, thus enhancing the possibility for significant energy mismatch between states. In identifying specific species for detailed study one should look for relatively small molecules in which the reaction coordinate appears to be localized in a bond involved in vibrational modes which are poorly coupled to a large fraction of the remaining molecular modes. These criteria point to kinetic systems which are undergoing rapid

reversible intramolecular conversions and are essentially at equilibrium at ambient temperatures. The kinetic parameters are then derived from measurements of relaxation times, either for natural fluctuations (spectral line-widths), or following perturbations externally imposed, at or below room temperature. It appears that the most sensitive tests for the adequacy of RRKM are the pressure dependencies of the rate constants at low pressure limits, where the mean times between collisions serve as an internal time scale for rates of intramolecular energy redistribution.

The following is a brief account of examples of each type which were recently investigated in our laboratory.

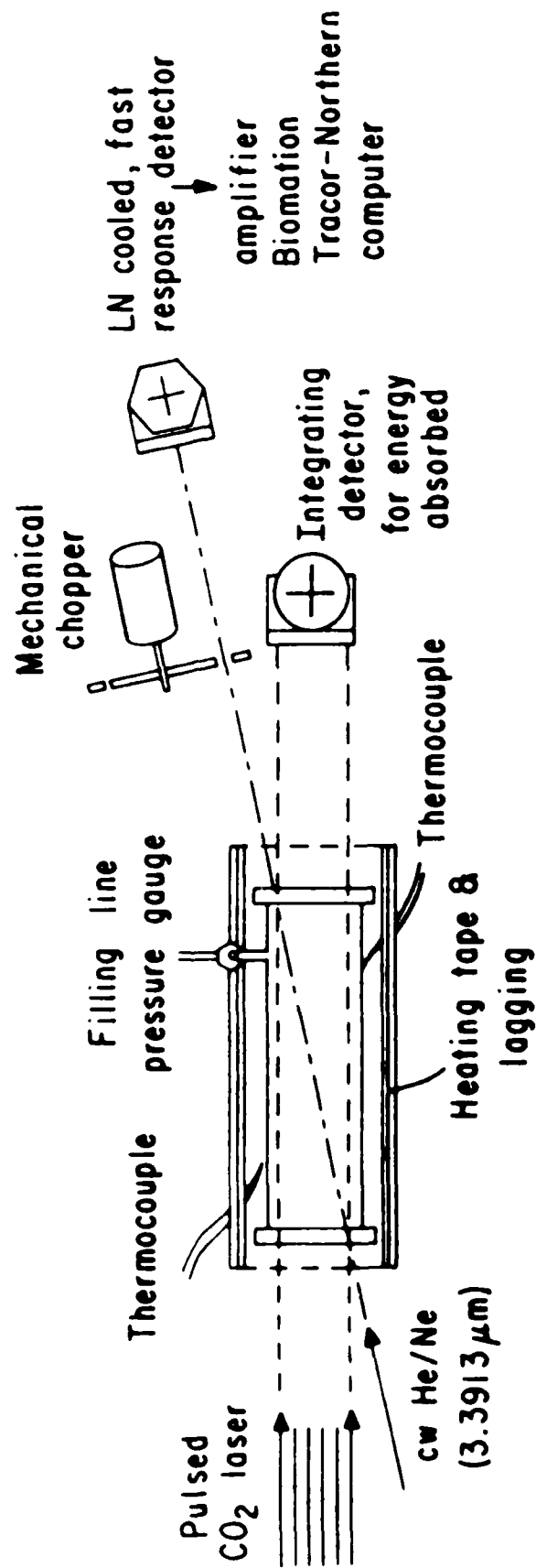
(i) Dissociation rates of dimeric formic acid in the gas phase were measured over the temperature range 293-335 K, via T-jump experiments. Since the He/Ne laser line at 3.3913  $\mu\text{m}$  is selectively absorbed by the dimer, changes in its intensity permit measurement on a  $\mu\text{s}$  time scale of relaxation times of dimer/monomer mixtures to their new equilibrium ratios, when perturbed by injection of small amounts of energy by a  $\text{CO}_2$  laser. Pulses ( $\approx 1 \mu\text{s}$  duration) from a line-tuned 750 mJ laser irradiated the experimental cell, which was temperature controlled, at IR frequencies which were absorbed either by the monomer or dimer. Initial formic acid pressures ranged from 1.0-2.75 Torr; these were kept low so that the entire length of the cell would be uniformly heated, and to avoid the generation of density oscillations induced by the steeply rising fronts of the irradiating pulses. Relaxation to equilibrium followed single exponential decays, which did not depend on whether the monomer or dimer was irradiated. [Figure 1 is a schematic of the experimental set-up.]

The thermochemical parameters for dissociation are well documented:  $\Delta H_{300}^0 = 14.14 \text{ kcal/mole}$  and  $\Delta S_{300}^0 = 36 \text{ eu}$ . However, the measured activation



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energy is  $6.8 \pm 1$  kcal/mole. Furthermore, even though at the pressures used the system should be in the 2nd order regime, the addition of (10-600) Torr of Ar had no measurable effect on the rate. These observations can be reconciled by assuming that (i) the ring structure opens when a (free) monomer adds to one of the O-HO bonds in the dimer, thereby releasing one of the initial monomers and generating a chain dimer; (ii) the latter relatively rapidly dissociates into two monomers. On this basis we predicted that other OH-bonding species would show a linear pressure dependence of the rate. This proved to be the case;  $(\text{CD}_3)_2\text{CO}$  is 0.036 as effective as  $\text{HCOOH}$ ;  $\text{THF-d}_8$  is 0.022 as effective as  $\text{HCOOH}$ ;  $\text{H}_2\text{O}$  is comparable to acetone but difficult to reproduce due to wall-adsorptions. These results are consistent with their relative H-bonding power.

(ii) The rate of bond inversion at the nitrogen atom in aziridine (dimethylene-imine) was measured in the gas phase for a range of pressures and temperatures.  $^1\text{H}$  NMR spectra were recorded of samples at 5-1100 torr, and from 298 to 388°K. Rate constants for inversion were derived by complete lineshape analysis of the NMR spectra. Their temperature dependence at the high pressure limit (1100 torr) gave  $E_a = 15.8 \pm 0.4$  kcal mole $^{-1}$ ;  $\Delta H^\ddagger = 15.2 \pm 0.4$  kcal mole $^{-1}$ ;  $\Delta S^\ddagger = -5.5 \pm 3$  e.u.; and  $\Delta G_{298}^\ddagger = 16.8 \pm 0.5$  kcal mole $^{-1}$ . These values are in excellent agreement with previously reported magnitudes obtained for solutions and in the gas phase at high pressures. However, at all temperatures we found no dependence of the first order rate constants on pressure down to 5 torr, in sharp contrast to the fall-off curves calculated with standard RRKM codes, which indicated that for pressures below 100 torr this system should be in the bimolecular regime. A less extended set of measurements was made with 2-methyl-aziridine which does show a small but clear fall-off in  $k_{\text{uni}}$ . These results can be rationalized in terms of the

regional phase space model, previously proposed for methylnitrite. In systems such as aziridine, where the density of states at the barrier height is sparse ( $\approx 10/\text{cm}^{-1}$ ) the rate of inversion is limited by the relaxation time for intramolecular vibrational energy redistribution. Our results indicate that many nanoseconds are required to attain relaxation, rather than picoseconds, estimated from the Marcus formula for  $k_{23}(E) = N^\ddagger(E^\ddagger)/h\rho(E)$ . In the methyl-substituted analog the barrier height is approximately 3 kcal mole $^{-1}$  higher, and the density of states at this barrier is higher than in aziridine. Relaxation data for conformational changes in  $\text{C}_6\text{H}_{12}$ ,  $\text{H}_3\text{CONO}$ ,  $\text{SF}_4$  and  $\text{C}_5\text{H}_{10}\text{O}$  were reanalyzed in terms of the regional phase-space model. At low pressures these also show departures from RRKM predictions.

Specific studies, in addition to the two examples cited, were reported in detail in the following publications:

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"Intramolecular Conversions Over Low Barriers. VII. The Aziridine Inversion - Intrinsically non-RRKM", D. B. Borchardt and S. H. Bauer, J. Chem. Phys., **85**, 4980-xxxx (1986).



"Resolution of Spectra of Mixtures, Applied to Gaseous Formic Acids", T. Wachs, D. Borchardt and S.H. Bauer, will be published in Spectrochimica Acta A.

"Conversions Over Low Barriers. VIII. The Mechanism & Rate of Dissociation of Dimeric Formic Acid", D. B. Borchardt and S. H. Bauer, submitted to J. Am. Chem. Soc.

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